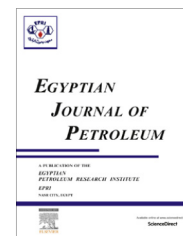




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REVIEW

Greener routes for recycling of polyethylene terephthalate



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Abstract The article reviews the different routes for recycling of polyethylene terephthalate. Chemical recycling processes are divided into six groups: methanolysis, glycolysis, hydrolysis, ammonolysis, aminolysis, and other methods. In a large collection of researches for the chemical recycling of PET, the primary objective is to increase the monomer yield while reducing the reaction time and/or carrying out the reaction under mild conditions. This article also presents the impact of the new recyclable catalysts such as ionic liquids on the future developments in the chemical recycling of PET.

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1. Synthetic polymers

The synthetic polymer industry represents the major end use of many petrochemical monomers such as ethylene, styrene, and vinyl chloride [1]. There are two main processes in the manufacture of synthetic polymers. The first involves breaking the double bond in the original olefin by additional polymerization to form new carbon–carbon bonds. For example, the fabrication of polyolefins, such as polyethylene and polypropylene, which is based on this general reaction. The second process is the elimination of water (or condensation)

between a carboxylic acid and an alcohol or amine to form polyester or polyamide [2].

Plastics are synthetic polymers that are divided into two groups: thermoplastics and thermo-set plastics [3]. Thermoplastics can be repeatedly softened and hardened by heating and cooling. In thermoplastics, the atoms and molecules are joined end-to-end into a series of long, sole carbon chains. These long carbon chains are independent of the others [4]. The structure in which the backbone is solely built of carbon atoms makes thermoplastics resistant to degradation or hydrolytic cleavage of chemical bonds. Consequently, thermoplastics are considered a non-biodegradable plastic. Examples of thermoplastics are polyethylene and polypropylene.

Thermo-set plastics are usually liquid or malleable prior to curing and designed to be molded into their final form. They are solidified after being melted by heating. The process of changing from the liquid state to the solid state is irreversible [3]. Distinguished from the linear structure of thermoplastics,

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thermo-set plastics have a highly cross-linked structure [3,2]. Since the main chain of thermo-set plastics is made of heteroatoms, it is possible that they are potentially susceptible to be degraded by the hydrolytic cleavage of chemical bonds such as ester bonds or amide bonds. Examples of this type are phenol-formaldehyde resin and polyurethane [5].

2. Polyethylene terephthalate (PET)

PET is semi-crystalline, thermoplastic polyester of characteristic high strength, transparency and safety [6]. For the manufacture of PET the intermediates, pure terephthalic acid (TPA) and ethylene glycol (EG), are derived from crude oil. When heated together the first product is a monomer bis(2-hydroxyethyl) terephthalate (BHET) mixed with low molecular weight polymers (oligomers). The mixture then reacts further, distills out excess ethylene glycol and forms the PET as shown in Fig. 1. At this stage, the PET is a viscous molten liquid. It is extruded, and water quenched to form a glasslike amorphous material. Some PET is also manufactured using technology based on the dimethyl ester of terephthalic acid (DMT).

The required high molecular weight PET is manufactured by a second polymerization stage carried out in the solid state at lower temperatures. This effectively removes all volatile impurities, like acetaldehyde, free glycols and water. The high molecular weight is essential for good mechanical properties providing stiffness, toughness and creep resistance while, at the same time, giving sufficient flexibility to resist bursting and breaking under pressure.

Once the polymer is formed it is very difficult to purify and for this reason the purity of the starting materials is the key factor. Vacuum distillation processes easily purify ethylene glycol while terephthalic acid is purified by repeated crystallization. Such high purity and high molecular weight materials are needed for food packaging applications.

Catalysts are used at extremely low concentrations to promote the reactions and ensure practical economics. The most common catalyst is antimony trioxide but salts of titanium, germanium, cobalt, manganese, magnesium and zinc are also used and small amounts remain encapsulated into the polymer matrix or in the polymer chain itself. However, in the laboratory, PET can be prepared by other reactions, such as the reaction of terephthaloyl chloride with ethylene glycol. This reaction is easier, but terephthaloyl chloride is more expensive than terephthalic acid, and it is more dangerous [7].

3. Importance of polyethylene terephthalate

PET has been traditionally employed in the production of textile fibers ever since the mid-1940s [8]. The PET bottle was patented in 1973 by Nathaniel Wyeth and began to be used popularly for the production of disposable soft drink bottles in the 1980s. In 1987, more than 700 million pounds of PET were consumed in their production [8].

The overall world production of polyesters was 25–30 million tons in 2000, this value increased to 55 million tons in 2012 and mostly consisted of polyethylene terephthalate (PET). Polyester consumption has increased substantially in fibers and molding resins due to the strong demand for textile

applications, as well as in food packaging and bottle markets for glass replacement [9].

Two PET grades now dominate the global market, i.e. fiber-grade PET and bottle-grade PET. These standard grades differ mainly in molecular weight or intrinsic viscosity (IV), respectively, optical appearance and the production recipes. The latter differ in the amount and type of co-monomers, stabilizers and metal catalysts, as well as colorants. Textile fiber-grade PET has a molecular weight of 15,000–20,000 g/mol, which refers to an intrinsic viscosity between 0.55 and 0.67 dL/g. PET fiber-grades for technical yarns such as tire cord have high molecular weights, with an intrinsic viscosity above 0.95 dL/g. Bottle-grade PET appears ‘glass-clear’ in the amorphous state. The average molecular weight ranges from 24,000 to 36,000 g/mol, which refers to an intrinsic viscosity between 0.75 and 1.00 dL/g. The standard bottle grade has an intrinsic viscosity of 0.80 dL/g. Other PET grades are manufactured for packaging films, as well as for the production of video and audio tapes. These PET types are often standard grades with an intrinsic viscosity of 0.64 dL/g. To reduce the sticking tendency of the final product, solid additives such as SiO₂ or clay with specific particle sizes and particle-size distributions are incorporated [10].

4. Recycling of waste polyethylene terephthalate

Recycling processes are the best way to economically reduce PET waste [11,12]. On the other hand, as the price of virgin PET remains stable, new and cheaper technologies for recycling PET give a benefit to the PET recycling industry by providing industry with relatively cheaper PET. The first recycling effort of post-consumed PET bottles in the world was in 1977 [13]. The major factor affecting the suitability of post-consumed PET flake for recycling is the level and nature of contaminants present in the flakes.

4.1. Contamination

Contamination of post-consumed PET is the major cause of deterioration of its physical and chemical properties during re-processing [14]. Minimizing the amount of these contaminants leads to better PET quality [15]. Post-consumed PET is contaminated with many substances such as the following:

4.1.1. Acid producing contaminants

The most harmful acids to the post-consumed PET recycling process are acetic acid, which is produced by poly(vinyl acetate) closures degradation, rosin acid and abietic acid that are produced by adhesives and hydrochloric acid that is produced by poly(vinyl chloride) (PVC). The acids act as catalysts for the chain scission reactions during post-consumed PET melt processing [16]. Paci and La-Mantia [17] reported that the presence of PVC (as little as 100 ppm) would increase post-consumed PET chain scission due to the catalytic effect of hydrogen chloride evolving during the degradation of PVC.

4.1.2. Water

Water reduces molecular weight (MW) during post-consumed PET recycling through a hydrolysis reaction. Moisture contamination should be below 0.02% to avoid the

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